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Study on the synthesis and ion-exchange properties of layered titanate $Na_2Ti_3O_7$ powders with different sizes

JUAN YANG*,†, DAN LI, XIN WANG, XUJIE YANG, LUDE LU
Materials Chemistry Laboratory, Center of Nanoscience and Nanotechnology, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China
E-mail: yangjuan6347@163.net

Layered titanate $Na_2Ti_3O_7$ powders with varying sizes were prepared by solid-state reaction of Na_2CO_3 and TiO_2 with different average particle sizes. The structures of the titanates and the products which had undergone H^+ and Ag^+ exchange were investigated by XRD, TEM and BET analysis. The influence of the particle size of starting material TiO_2 on the reaction rate, the particle size and ion-exchange property of the resulting products was studied. It is found that nanometer sized TiO_2 facilitates the solid-state reaction and leads to the formation of ultrafine titanate. The H^+-exchange property is improved by decreasing the particle size of $Na_2Ti_3O_7$ and the small sized layered titanate can be exfoliated easily by $AgNO_3$ solution. © *2003 Kluwer Academic Publishers*

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1. Introduction

A number of layered titanates with interlayer alkali metals have received considerable attention because of their potential application in various technologies as ion exchangers, adsorbents, photocatalysts and catalyst supports [1–5]. Recently, various nanocomposites have been formed via the intercalation of new species (e.g., CdS, PbS, Fe_2O_3, TiO_2, SiO_2 and Al_2O_3) into the interlayer space for photocatalysis applications [6–11]. The exfoliated nanosheets of these compounds have also been used as building blocks to construct self-assembly multilayers with excellent optical property [12–14]. Compared with nature layered materials such as montmorillonite and smectite clays, the intercalation and delamination of layered titanates are not easy to achieve because of their high charge density. So far, only cesium titanate ($Cs_xTi_{2-x/4}\square_{x/4}O_4$) has been reported to be exfoliated into their elementary nanosheets owing to its relatively low charge density [15–17]. Therefore, it is interesting to study the intercalation and delamination ability of the layered titanates.

It is known that the properties of materials may be influenced by the sizes, and particular properties differing from that of the bulk materials may appear as the dimension is reduced to submicrometer or nanometer scale [18]. For layered materials, Leroux suggested that the charge density might be influenced by the specific surface areas, in another word, by the particle size of the materials [19]. So we considered that the intercalation and delamination properties of layered titanates might also be influenced by the particle sizes of the titanates, though this has received little attention. Currently, layered titanates are at micrometer size because they are usually prepared via a solid state reaction at high temperatures (800–1300°C) with long reaction times [1, 20]. To our knowledge, because of the difficulty in preparing layered titanates with varying sizes, the influence of the particle size on the intercalation and delamination properties has never before been reported.

As mentioned above, the layered titanates are usually prepared by solid-state reaction and it is well known that the solid-state reaction initiates at the contact surface of the reactants, and the reaction may be improved by decreasing the sizes of the reactants. Our previous study also showed that nanostructured precursors may accelerate the solid state reaction and also lead to the formation of nanoscaled complex oxides [21–23]. So we considered that the particle sizes of layered titanates might be controlled by the particle sizes of the reactants.

In this paper, layered $Na_2Ti_3O_7$ powders with varying sizes are obtained by changing the particle size of raw material TiO_2 using solid-state reaction; the influence of the particle size of $Na_2Ti_3O_7$ powders on the ion-exchange and exfoliation properties is also investigated.

2. Experimental

Anatase structured titanium dioxide powders with different average particle sizes (their TEM images showed

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*Author to whom all correspondence should be addressed.

†*Present address*: School of Materials Science & Engineering, Jiangsu University, zhenjiang, jiangsu 212013, People's Republic of China.

the average particle sizes were approximately 20 nm, 200 nm and >1 μm, respectively) were supplied by Taixing Nanometer Material Factory, China. The purity is higher than 99%. Analytical purity Na_2CO_3 was obtained from Hongguang Chemistry Factory of Shanghai, China.

$Na_2Ti_3O_7$ powders were prepared by heating a mixture of Na_2CO_3 and TiO_2 in a molar ratio of 1:3 at 800°C for 60 h and the mixture was ground every 20 h. $H_2Ti_3O_7$ was obtained by removing Na^+ of $Na_2Ti_3O_7$ (ca. 1 g) in 1000 ml 0.5 M HCl at 60°C for 3 days. The acid solution was renewed everyday in order to remove Na^+ completely from the compounds. The products were washed with distilled water and dried in vacuum at 30°C. For Ag^+-$H_2Ti_3O_7$, 1 g $H_2Ti_3O_7$ was soaked in 25 mL 1 M $AgNO_3$ solution at 25°C for several days, the products were washed with distilled water and dried in vacuum at 30°C. Corresponding to the raw TiO_2 with varying particle sizes (20 nm, 200 nm, >1 μm), the obtained products were denoted as $Na_2Ti_3O_7$(I), $Na_2Ti_3O_7$(II), $Na_2Ti_3O_7$(III), $H_2Ti_3O_7$ (I), $H_2Ti_3O_7$(II), $H_2Ti_3O_7$(III) and Ag^+-$H_2Ti_3O_7$(I), Ag^+-$H_2Ti_3O_7$(II), Ag^+-$H_2Ti_3O_7$(III), respectively.

Powder X-ray diffraction (XRD) patterns were obtained on a Bruker D8 ADVANCE diffractometer using monochromatized Cu K_α ($\lambda = 0.15405$ nm) irradiation. TEM images were obtained with an H-800 microscope using 175 KV accelerating voltage. The BET specific surface areas of the samples were obtained by nitrogen adsorption/desorption isotherms at liquid nitrogen temperature (77 K) using Micromeritics ASAP 2010C instrument.

The chemical composition of the powders was characterized by chemical analysis, which was carried out as follows: The solid phases were dissolved by concentrated sulfuric acid and ammonium sulfate with heating. The sodium content was determined by atomic absorption spectrophotometry, and the titanium content was determined by the H_2O_2 color development reaction using UV-1100 UV-Vis spectrometer.

In order to compare the H^+-exchanging rate of the three $Na_2Ti_3O_7$ samples, the samples (1.5 g) were first soaked in 130 ml 0.06 M HCl at 40°C and then the solution was agitated at a constant rate to accelerate the exchange process. The relationship of the concentration of H^+ in the solution with time was recorded using a pHS-2C accurate acidimeter.

For Ag^+ concentration measurement, 0.1 g $H_2Ti_3O_7$ sample was added to 25 ml 0.06 M $AgNO_3$ solution, stirred at 25°C until the Ag^+ concentration did not change. The Ag^+ concentration in the suspension was detected by an Ag^+ selective electrode using a UJ33A electric potential difference meter.

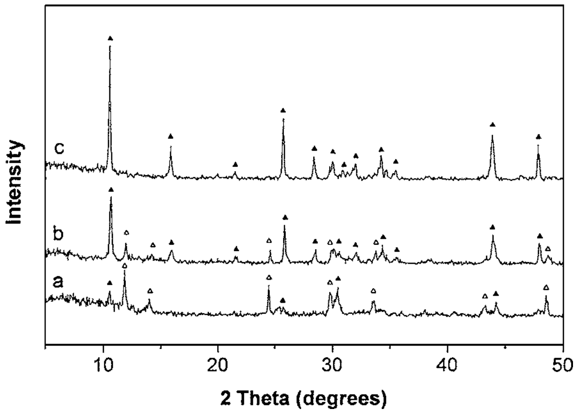

Figure 1 XRD patterns of the mixture of (20 nm)TiO_2 with Na_2CO_3 calcined at different conditions: (a) 750°C 5 h, (b) 750°C 26 h, and (c) 800°C 8 h (△: $Na_2Ti_6O_{13}$; ▲: $Na_2Ti_3O_7$).

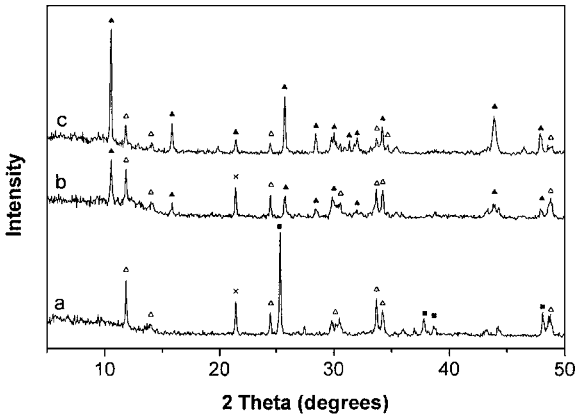

Figure 2 XRD patterns of the mixture of (>1 μm)TiO_2 with Na_2CO_3 calcined at different conditions: (a) 750°C 5 h, (b) 750°C 26 h, and (c) 800°C 8 h (■: TiO_2; △: $Na_2Ti_6O_{13}$; ▲: $Na_2Ti_3O_7$; ×: unknown phase).

3. Results and discussion

According to the XRD experiments, the solid-state reaction was accelerated by decreasing the particle size of the raw material TiO_2. And the results are shown in Figs 1, 2 and Table I. In the reaction system of (20 nm) TiO_2, pure $Na_2Ti_3O_7$ (JCPDS 31-1329) was obtained after the mixture calcined at 800°C for 8 h. But in the system of (>1 μm) TiO_2, $Na_2Ti_3O_7$ and the intermediate phase $Na_2Ti_6O_{13}$ (JCPDS 14-277) coexisted when the mixture calcined at 800°C for 8 h and pure $Na_2Ti_3O_7$ was only obtained after the mixture further calcined at 800°C for more than 40 h. So it can be concluded that the preparation period of $Na_2Ti_3O_7$ can be reduced by using nanometer sized TiO_2. Furthermore, in the system of (>1 μm) TiO_2, an unknown peak of $2\theta = 21.5°$ appeared at the beginning of the solid-state reaction and the intensity decreased as the reaction proceeded;

TABLE I XRD results of the reaction products calcined at different conditions (3NaTi and 6NaTi represent $Na_2Ti_3O_7$ and the intermediate phase $Na_2Ti_6O_{13}$, respectively)

Reaction system	750°C 2.5 h	750°C 5 h	750°C 26 h	800°C 8 h	800°C 16 h	800°C 40 h
(20 nm)TiO_2 + Na_2CO_3	TiO_2 + 6NaTi	6NaTi	6NaTi + 3NaTi(main)	3NaTi		
(200 nm)TiO_2 + Na_2CO_3	TiO_2 + 6NaTi	6NaTi	6NaTi + 3NaTi(main)	6NaTi(little) + 3NaTi	3NaTi	
(>1 μm)TiO_2 + Na_2CO_3	TiO_2	TiO_2 + 6NaTi	6NaTi + 3NaTi	6NaTi + 3NaTi(main)	6NaTi(little) + 3NaTi	3NaTi

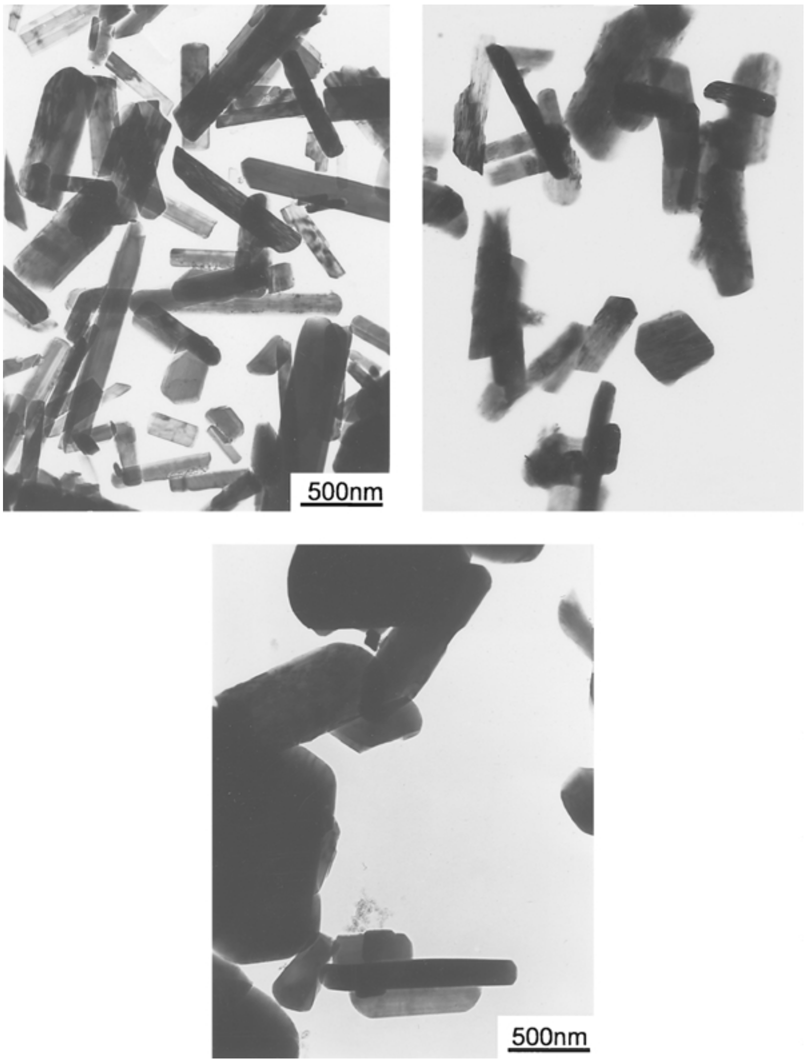

Figure 3 TEM micrographs of (a) $Na_2Ti_3O_7$(I), (b) $Na_2Ti_3O_7$(II), and (c) $Na_2Ti_3O_7$(III).

this indicated that the reaction mechanism might also be influenced by the particle size of the raw material TiO_2.

Small sized TiO_2 causes higher reaction rate and higher reaction rate may cause large amount of crystalline nuclei to form in a short time and inhibit the growth of crystals. So the particle sizes of TiO_2 may also influence the particle sizes of the resulting products. Fig. 3 shows the TEM images of the obtained $Na_2Ti_3O_7$ samples. All three products are sheet-like but with different particle sizes. $Na_2Ti_3O_7$(I) is the smallest with the average size of 150 nm × 1.2 μm, $Na_2Ti_3O_7$(II) 250 nm × 1.1 μm while $Na_2Ti_3O_7$(III) is severely aggregated.

In addition, the decrease of the particle size of layered titanates will lead to the increase of their surface areas. Actually, the specific surface areas of $Na_2Ti_3O_7$(I–III) were 11 $m^2\,g^{-1}$, 8.6 $m^2\,g^{-1}$ and 4 $m^2\,g^{-1}$, respectively. The high specific surface area is attractive in the catalytic application [24].

Although the particle size of TiO_2 can influence the solid-state reaction rate and the particle sizes of the resulting products, but it has little effect on the structure of the resulting $Na_2Ti_3O_7$ powders which can be confirmed by the XRD experiments and the chemical analysis results. The three XRD patterns of pure $Na_2Ti_3O_7$ samples listed in Fig. 4 are almost the same, which is in agreement with the result reported in [1]. Chemical analysis results are listed in Table II. Almost the same content of elements Na and Ti indicate that the chemical composition of the three $Na_2Ti_3O_7$ samples are not influenced by the particle sizes of TiO_2. So $Na_2Ti_3O_7$ powders with the same crystalline structure but different particle sizes can be obtained by controlling the particle size of the starting material TiO_2 and the particle

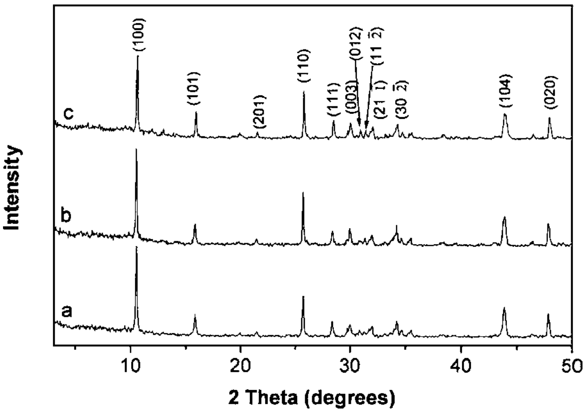

Figure 4 XRD patterns of (a) $Na_2Ti_3O_7$(I), (b) $Na_2Ti_3O_7$(II), and (c) $Na_2Ti_3O_7$(III).

TABLE II Results of chemical analysis of $Na_2Ti_3O_7$ and $H_2Ti_3O_7$ samples

	$Na_2Ti_3O_7$			$H_2Ti_3O_7$		
	(I)	(II)	(III)	(I)	(II)	(III)
Content of Na (mass%)	15.2	15.2	15.1	0.5	0.5	0.7
Content of Ti (mass%)	46.2	46.4	46.8	54.5	54.2	54.5

size of $Na_2Ti_3O_7$ powders will further influence their properties.

Ion exchange property is one of the most important properties of layered titanates because the intercalation reaction is often performed by series ion-exchange reactions. The H^+-exchange property of $Na_2Ti_3O_7$ samples was influenced by the sizes of $Na_2Ti_3O_7$ powders. Fig. 5 shows the relationship of the H^+ concentration ($[H^+]$) with duration time when $Na_2Ti_3O_7$ powders were added into 0.06 M HCl solution. In all three $Na_2Ti_3O_7$-HCl system, $[H^+]$ in the solution decreased with the duration time. Compared with $Na_2Ti_3O_7$(III)-HCl system, $[H^+]$ decrease rate is higher in both the $Na_2Ti_3O_7$(I)-HCl and the $Na_2Ti_3O_7$(II)-HCl systems. The exchange rate of $Na_2Ti_3O_7$(I)-HCl system is the highest. This result suggests that the H^+-exchange rate is dependent on the size of $Na_2Ti_3O_7$. Results of chemical analysis of H^+ exchanged samples are also listed in Table II. After H^+-exchanging reaction (0.5 M HCl, 60°C, 3 days), the three products all contain a negligible amount of Na^+, which suggests that although the particle size of $Na_2Ti_3O_7$ influenced the H^+-exchanging rate, it had little effect on the resulting H^+-exchanging extent. According to the chemical analysis, the ideal composition of the H^+ exchanged product is $H_2Ti_3O_7$. Fig. 6d shows the XRD pattern of $H_2Ti_3O_7$(I) which is also in agreement with the result reported in [1].

Besides the H^+-exchanging property, Ag^+-exchanging property was also studied because Ag^+ loaded titania is a good photocatalyst [25]. In our experiment, it was found that the $H_2Ti_3O_7$ could be exchanged by Ag^+ directly in 1 M $AgNO_3$ solution, and its Ag^+-exchange property was also influenced by the sizes of the titanates.

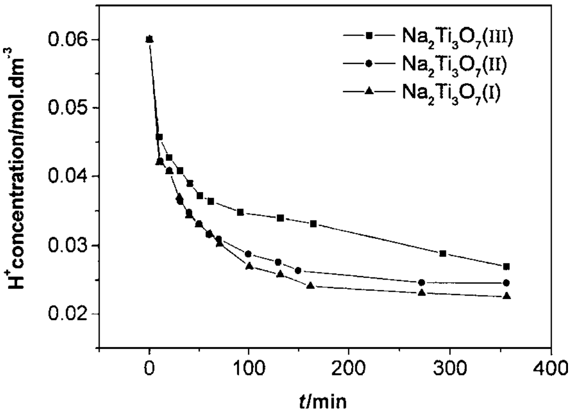

Figure 5 Change of H^+ concentration with time when $Na_2Ti_3O_7$ powders were reacted with 0.06 M HCl solution.

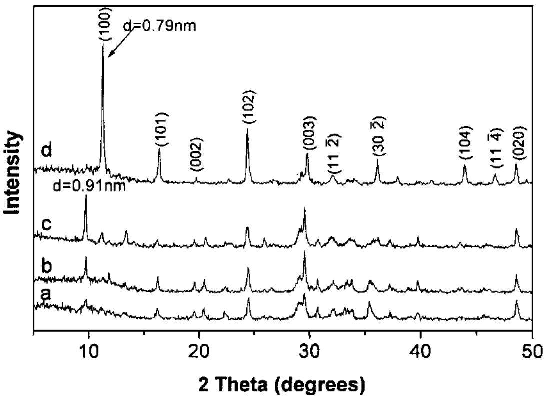

Figure 6 XRD patterns of $H_2Ti_3O_7$ reacted with 1 M $AgNO_3$ for 30 days: (a) Ag^+-$H_2Ti_3O_7$(I), (b) Ag^+-$H_2Ti_3O_7$(II), (c) Ag^+-$H_2Ti_3O_7$(III), and (d) $H_2Ti_3O_7$.

Fig. 6 shows the XRD patterns of $H_2Ti_3O_7$ reacted with $AgNO_3$ solution for 30 days. In Fig. 6c, two immiscible phases are present. One phase with an interlayer distance of 0.79 nm is attributed to $H_2Ti_3O_7$ (Fig. 6d). The other phase with an interlayer spacing of 0.91 nm is Ag^+-partially loaded phase. In Fig. 6a, the peak of $d = 0.79$ nm has disappeared and the intensity of low-angle peak ($2\theta = 9.8°$, $d = 0.91$ nm) is much lower than that in Fig. 6b, c, but the sharper, higher angle ($>16°2\theta$) peaks are comparable to those of $H_2Ti_3O_7$. This is quite similar to the results in [26], implying that most of $H_2Ti_3O_7$(I) was exfoliated. In Fig. 6, the intensity of the peak ($d = 0.91$ nm) decreases with decreasing particle size of the $H_2Ti_3O_7$ samples, indicating that the delamination property of the sample is improved by decreasing the particle size. This can also be confirmed by the Ag^+ concentration remaining in the solution. Ag^+ is exchanged into the interlayer space, the Ag^+ remaining in the suspension would increase when most of the host layers are exfoliated into nanosheets. The detected results were in accordance with this analysis that the Ag^+ remaining in the solution of $H_2Ti_3O_7$ (I–III) were 81.7%, 71.7% and 68.4%, respectively.

Since the exfoliated nanosheets are attractive, many researchers are studying the methods to delaminate layered oxides [27]. The strategy reported herein to prepare ultrafine layered oxides using nanoscaled raw materials makes it possible to delaminate the compounds quickly and successfully. It is also well known that particular properties differing from bulk materials may appear as the dimension of materials is reduced to submicrometer or nanometer scale. So the prepared nanocomposite or multilayers from ultrafine layered compounds may also exhibit some new properties differing from those conventionally prepared. Further study of this area may be of interest.

4. Conclusions

Titanate $Na_2Ti_3O_7$ powders with varying sizes were prepared via solid-state reaction by using TiO_2 with varying average particle sizes, ultrafine $Na_2Ti_3O_7$ with high specific surface areas was prepared by using nanometer-sized TiO_2 as the reactant. The solid-state reaction rate and H^+-exchange rate was increased by decreasing the particle size of the starting material, TiO_2. The resulting product $H_2Ti_3O_7$ could be exchanged by Ag^+ and the smaller sized $H_2Ti_3O_7$ allowed the layered structure to be exfoliated easily. These results suggest that the properties of layered compounds might be size dependent and a way to improve the intercalation or exfoliation ability of layered compounds may be by decreasing their particle sizes.

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